L = property of the liquid
w = property of water
1 = condition of system 1
2 = condition of system 2

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Manuscript received April 8, 1980, revision received April 13 and accepted April 23, 1981

Kinetics of Coal Drying-Decomposition

G. G. KARSNER and
D. D. PERLMUTTER

Department of Chemical Engineering
University of Pennsylvania
Philadelphia, PA 19104

A series of seven coals of different ranks and from various locations were heated in an inert atmosphere under relatively mild conditions to measure the rates of gas evaporation. Samples crushed to various fractions in the particle size range −6 +50 U.S. mesh were studied at temperatures in the range of 150 to 300°C. The results show that: (1) most water is released at 100°C, evidently an evaporation process, (2) CO_2 is evolved at 150°C and above, and (3) CO is evolved at 250°C and above. An interpretive model was developed to fit the CO_2 production rate and kinetic constants were obtained. Gas evolution rates are independent of particle size for the most porous coals, but vary among coals, depending on both chemical composition and physical structure. A 15% loss in heating value was incurred during drying and subsequent oxidation when the pretreatment temperature was increased from 150 to 225°C.

SCOPE

The rates at which gases are evolved during coal drying under an inert atmosphere were measured in a fixed bed reactor. Seven coals from different sources were crushed to the particle size range −6+16 U. S. mesh and dried under isothermal conditions at 150°C. Four of the coals were further tested for particle size and temperature effects. The effects of drying severity on subsequent oxidation rates were also measured. The dried coals were analyzed for changes in chemical composition and heating value. A model was developed and kinetic parameters were estimated for the carbonic gas evolution rate.

CONCLUSIONS AND SIGNIFICANCE

As a result of experimental drying tests on seven coals from different sources, it has been found that (1) water is released mainly as the result of an evaporative process at 100°C, (2) CO_2 is produced under an inert atmosphere at temperatures as low as 150°C, and (3) CO is produced at 250°C and higher temperatures. The carbonic gases are evidently produced as the result of thermal decomposition of oxy-functional groups on the coal surfaces, since CO_2 production rate increases with the original oxygen content of the coal. A drying model that assumes zero and first order decompositions of oxy-functional groups fits the data, providing activation energies as low as 13 to 22 MJ/kmol for CO_2 production. Gas evolution rates are independent of particle size for a given coal, indicating that the relatively low activation energies are not the result of diffusional limitations. The oxidation rate of the lignite coal tested was found to be quite sensitive to prior drying temperature: the rate at 150°C doubled when the coal was dried at 300°C instead of 150°C.

The oxidative pretreatment of coal to reduce or eliminate its swelling and caking propensity consists of two steps: (1) coal drying while the coal is heated to pretreatment temperatures and (2) coal oxidation. These steps, usually performed simultaneously, include both rapid heating and addition of gaseous oxygen. The first step is often taken for granted by assuming that the thermal drying involves only the removal of water; thus the two steps are studied as one. Since for design and optimization of an oxidative pretreatment process knowledge of low temperature drying kinetics is useful, this study was undertaken to isolate the drying step as separate from the oxidative pretreatment and to examine possible chemical as well as physical changes which may occur.

Coals may contain large quantities of water; lignites often contain water in excess of 20 weight percent. Prior to oxidizing coals, water is typically removed in the laboratory by either (1) heating

ISSN-0001-1541-82-5221-0199-$2.00

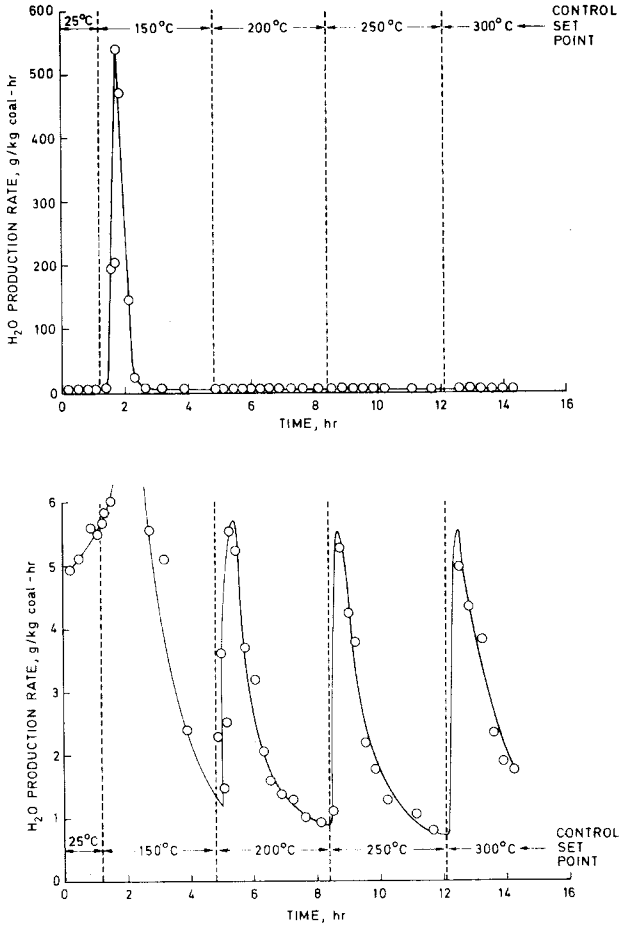

Figure 1. Effect of drying temperature on H_2O production rate. Coal: lignite, PSOC 87; particle size: −6 +16 U. S. mesh; gas flow: 200 cm^3/min N_2.

the coal sample in an inert atmosphere or (2) evacuating the coal sample. This preliminary step is used to experimentally differentiate between the evolution from the coal particles of naturally occurring water and water produced by chemical reaction during oxidation. Several ASTM Standard methods for the determination of the water content of coals are summarized by Volborth (1976). Results can differ with test conditions.

Panaseiko (1974) characterized the various states of water in coal as "chemically bound, sorption-bound, or free." The chemically bound water is linked to the coal predominately through hydrogen bonds to oxygen-containing groups on the coal surfaces. The amount of water physically adsorbed on the coal is determined by the "orientation, dispersion, and induction forces of intermolecular interaction." Rukin and Gorskaya (1974) pointed out that lignites often contain a much larger quantity of water than coals of other rank. They attributed the difference in water content to the chemical structure of the lignite, in particular the oxy-functional groups on its surfaces which form hydrogen bonds with water molecules. They postulated the formation of multiple hydrogen bonds between water molecules and individual —OH and —COOH sites on the coal. Artificial blocking of these oxygenated groups with chemical agents result in less so-called "bound" water. Coals treated with these blocking agents dry more quickly since a larger percentage of the water is in a free state than is bound. Parkash (1974) also concluded that water molecules become secondary adsorption centers for additional hydrogen bonding with successive water molecules.

In addition to water evolution during coal drying, several decomposition reactions accompanying a thermal coal treatment, producing H_2O, CO_2, and CO (Allardice and Evans, 1971 a,b). Such pyrolysis reactions have been studied to temperatures in excess of 1000°C. Fitzgerald and van Krevelen (1959) heated eight coals of varying rank at a rate of 1.8°C/min up to 730°C, measuring the quantities of hydrocarbons evolved up to C_4. Virtually no hydrocarbon gases were produced below 350°C. In the 400 to 700°C temperature range, the major products were hydrogen and methane. Only trace quantities of CO and CO_2 were produced. They postulated that CO_2 comes primarily from carboxyl groups while CO is the decomposition product of carbonyl groups and ether linkages. Some water is also produced by chemical reaction from peripheral hydroxyl and hydrogen sites. Hydrocarbon gases were assumed to be formed from dual-site interactions on the solid surfaces. Several types of oxy-sites have been reported, usually associated with oxygen adsorption during mild coal oxidation. These functional groups include: carboxyl, hydroxyl, carbonyl, methoxyl, esters, ethers, peroxides, and hydroperoxides (Adams and Pitt, 1955; Blom et al., 1957; Mukherjee and Lahiri, 1957; Bhowmik et al., 1959; Mazumdar et al., 1959; Marinov, 1977; and Kucher et al., 1977).

Campbell (1978) heated a western (Wyodak) subbituminous coal from 110 to 1000°C under an inert argon atmosphere at reduced pressure. Only trace quantities of CO_2 and CO evolved at 250°. Hydrogen and hydrocarbon gases were produced starting around 400°C. Campbell suggested that CO_2 is produced by the decomposition of carboxyl groups below 520°C and carbonate decomposition above this temperature. He agreed with Fitzgerald and van Krevelen's (1959) conclusion that CO comes primarily from carbonyl groups and ether links.

In summary, the following conclusions may be drawn from the literature about coal drying in an inert atmosphere or under vacuum below 300°C:

1. The major gases produced are H_2O, CO_2, and CO.
2. Little or no hydrocarbons are produced at these temperatures.
3. CO_2 and CO evolution are the result of the decomposition of existing oxygenated groups on the coal surfaces.
4. Gas evolution rate is highly dependent upon the chemical composition of the coal.

EXPERIMENTAL

For the purposes of this study, samples of seven coals were obtained from the DOE-Penn State Coal Bank and dried in a fixed bed reactor. The samples were of various ranks including one anthracite (PSOC 80), five bituminous coals (PSOC 4, 127, 135, 190, 197), and one lignite (PSOC 87). Chemical compositions were reported earlier by Avison et al. (1979), ranging from 65 to 84% carbon, 3 to 20% oxygen, and 1 to 28% moisture. Total porosities varied over seven-fold between 0.033 and 0.232 cm^3/g, CO_2-surface areas between 96 and 408 m^2/g.

The coals were dried under various conditions to examine the effects of coal porosity, particle size, chemical composition, and drying temperature. The stainless steel reactor (711 mm in length and 19 mm OD) was fitted with top and bottom thermocouples, and the effluent line was connected to a Hewlett-Packard Model 5830 A gas chromatograph. A sample of 45 g of coal sieved to various screen cuts produced a bed height of about 30 cm. After purging the fixed bed reactor at ambient temperature with 4.4 liters/min of flowing nitrogen, the reactor was heated to the set point drying temperature at a rate of 4 to 5°C/min. Gas analyses for CO and CO_2 were performed every 20 minutes. Water measurements were cumulative by weight of in-line anhydrone driers. Further details of the experimental equipment were given by Kam et al. (1976).

RESULTS AND DISCUSSION

Among the seven coals of different rank and from diverse sources that were studied to delineate their similarities and differences with respect to moderate temperature drying kinetics, the most striking result is that significant amounts of CO_2 and CO are produced in addition to water when drying under an inert atmosphere in the temperature range from 150 to 300°C. To determine the rate of gas evolution when thermally dried prior to oxidation, the coal with the highest water content in this study (a lignite, PSOC 87, 22.7% water) was dried in the fixed bed reactor. After purging with nitrogen at 25°C the coal was heated in 50°C steps from 150°C to 300°C during a continuous 14-hour drying run. The rates of water

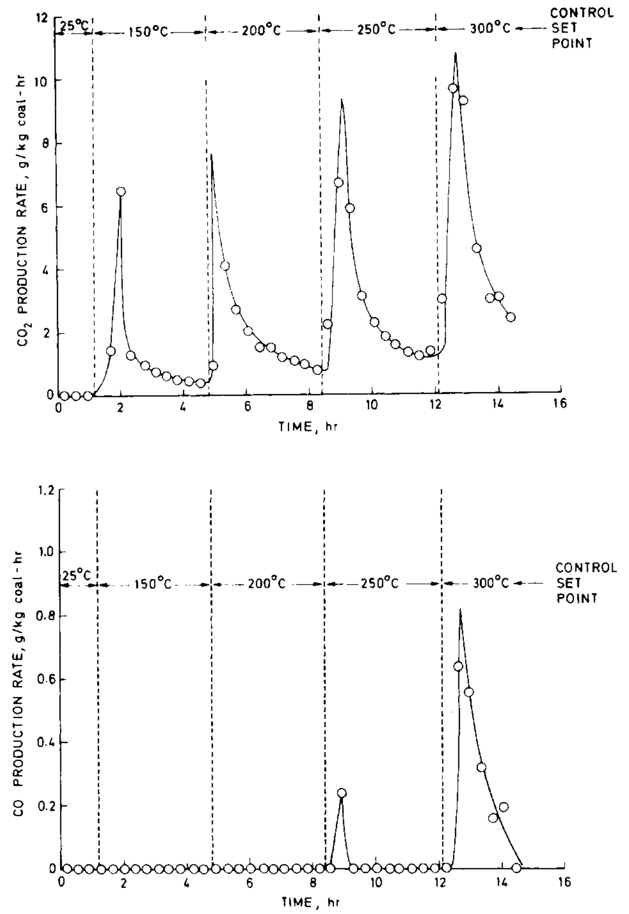

Figure 2. Effect of drying temperature on CO_2 and CO production rates. Coal: lignite, PSOC 87: particle size: −6 +16 U. S. mesh; gas flow: 200 cm^3/min N_2.

production at these temperatures are given in Figure 1 on each of two ordinate scales. The rate was always less than 6 g/kg coal-hr with the exception of a large release of water which occurred when the reactor temperature was raised from 25 to 150°C. This single peak accounts for most of the original water in the sample. The maximum rate of 540 g/kg coal-hr occurs at approximately the time when the reactor temperature reaches the boiling point of water. These findings imply that most water production is merely the result of evaporation. Small increases in the water production rate occur when reactor temperature is increased in 50°C increments above 150°C, as shown in the lower graph in Figure 1, where the sensitivity of the ordinate is increased 100-fold. Additional small amounts of water are released from the coal at the successively higher temperatures even though the rate decays to 2 g/kg coal-h or less during each isothermal operation.

As presented in Figure 2 significant amounts of CO_2 were also released at these relatively low temperatures. Although no CO_2 was produced at room temperature, detectable quantities were observed at temperatures as low as 150°C; further, although the rate of CO_2 production decreases with time during isothermal operation, the maximum rate increases at each successively higher temperature. Gas analysis for CO is also presented in Figure 2 to show that CO is formed in smaller quantities than CO_2 and only at the higher reaction temperatures of 250 and 300°C. The rate of CO production also decreases rapidly with time for each isothermal operation. Similar results were observed when the test was repeated with HVC bituminous coal, PSOC 190. Between 200 and 325°C Kam (1975) found no evidence of carbonic gas formation when isothermally drying an HVA bituminous coal (Pittsburgh Seam) under nitrogen for a period of one hour. He concluded that any CO_2 or CO detected in the reactor effluent gases during oxidation must be oxygenated products and not the result of the thermal degradation of coal. In view of the current results, it is clear that gas evolution must be characterized for each coal.

TABLE 1. POTENTIAL CO_2 FORMATION FROM TRAPPED AIR

Coal, PSOC No.	Total Porosity,* cm^3/g	Maximum cm^3 Air in 45 g Coal	Potential CO_2 Evolved from Trapped Air, g
190	0.232	10.4	0.0410
87	0.105	4.7	0.0019
197	0.105	4.7	0.0019
80	0.076	3.4	0.0130
127	0.052	2.3	0.0009
135	0.042	1.9	0.0007
4	0.033	1.5	0.0006

* From Gan, Nandi and Walker (1972).

Source of Oxygen

The source of the oxygen in the carbonic gases evolved during coal drying is a question of some interest. Since the feed gas used in these experiments was ultra-high purity nitrogen (99.995%), the oxygen emerging in the carbonic gases cannot come from this source. The oxygen must therefore be derived from the coal unless

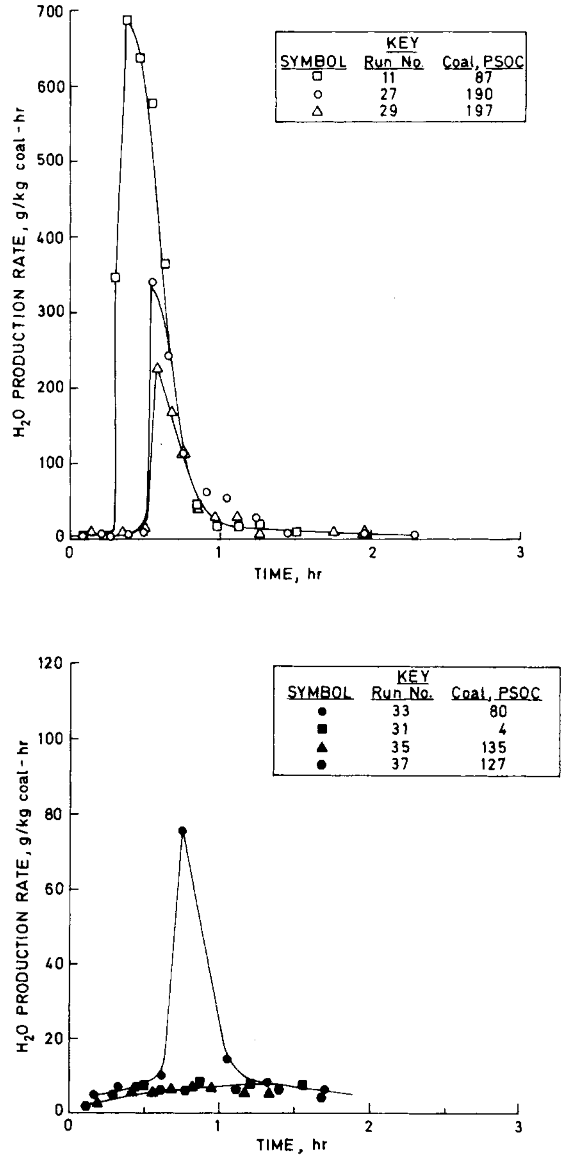

Figure 3. Rate of H_2O production during drying of different coals. Particle size: −6 +16 U. S. mesh; gas flow: 200 cm^3/min N_2; temperature: 150°C.

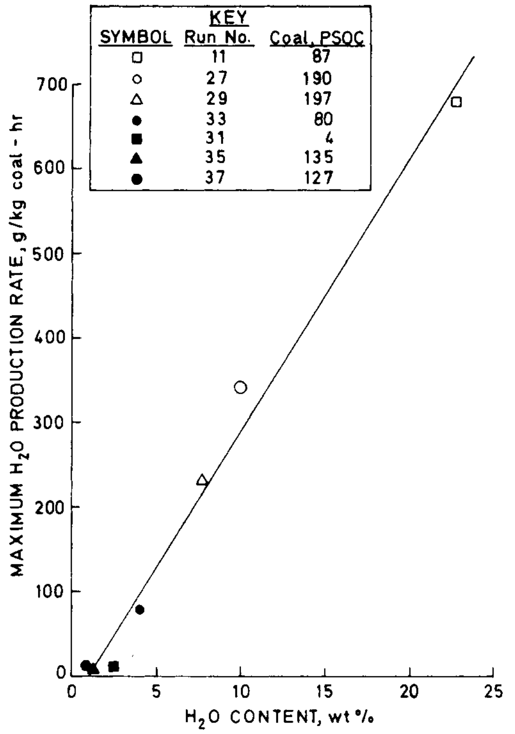

Figure 4. Effect of initial H_2O content on maximum H_2O production during drying. Particle size: −6 +16 U. S. mesh; gas flow: 200 cm^3/min N_3; temperature: 200°C.

it can be shown that sufficient air can be trapped within the coal pore structure to react to form the observed carbonic gases. Such an estimate requires the pore volume information listed in Table 1 for the seven coals used in this study. The trapped air can never exceed the total pore volume of the 45 g bed of coal used in each experiment. Table 1 shows the stoichiometrically equivalent amount of CO_2 which could be formed from these volumes of air. For comparison, the cumulative CO_2 produced during the 14-hour run, represented by the total area under the CO_2 rate curve (e.g., Figure 2) is approximately 1.46 g CO_2 for PSOC 87 and 0.50 g CO_2 for PSOC 190, showing that the CO_2 formed from the trapped air cannot account for more than 10% of the CO_2 formed for PSOC 190 or more than 0.1% of the CO_2 formed for PSOC 87. It may be concluded that the oxygen in the carbonic gases comes primarily from the solid coal.

Effect of Coal Type

The rate of gas evolution during coal drying prior to or in conjunction with oxidation, depends upon the unique combination of chemical composition and physical structure of each individual coal. The solid species is the only reactant when drying in an inert atmosphere, and as shown above, the oxygen in the carbonic gases is derived from oxygen-containing groups in the coal. To determine the effect of coal type on H_2O and CO_2 evolution, a set of drying runs were performed on the seven coals under replicate conditions of 150°C and particle size −6+16 U. S. mesh. The water production rates are presented in Figure 3. Each coal with at least 3.9 percent water produced a single large peak as the coal was heated from 25 to 150°C. Each rate then decayed rapidly toward zero. As shown in Figure 4, the maximum rate of water production that occurred in each case at approximately 100°C is linearly dependent on the original water content of the coal. The correlation coefficient is 0.99 for the least squares line shown.

Of equal importance to the rate of water removal during the drying process is the physical location and chemical nature of the water initially on the coal. With this in mind it is of interest to compare the water volume with the porosity of each coal. With the exception of the lignite, the water in the coal occupies an equivalent volume which is less than the total porosity, assuming the water retains its density at 1.0 g/cm^3. However, for the lignite, which contains 22.7 weight percent water, less than half of this water can be contained within the pore structure and the rest must be distributed on the coal surfaces. The water content of the coals in this study increases with the coal oxygen content, supporting the idea of Rukin and Gorskaya (1974) that most of the water in a lignite is hydrogen bonded to oxy-functional groups on the coal such as R—OH and R—COOH, as well as the argument of Parkash (1974) that hydrogen bonds may be formed between water molecules, where one is attached to an oxy-containing group on the coal. The water content of a coal is therefore affected by both its physical (pore volume) and chemical structure (oxygen content).

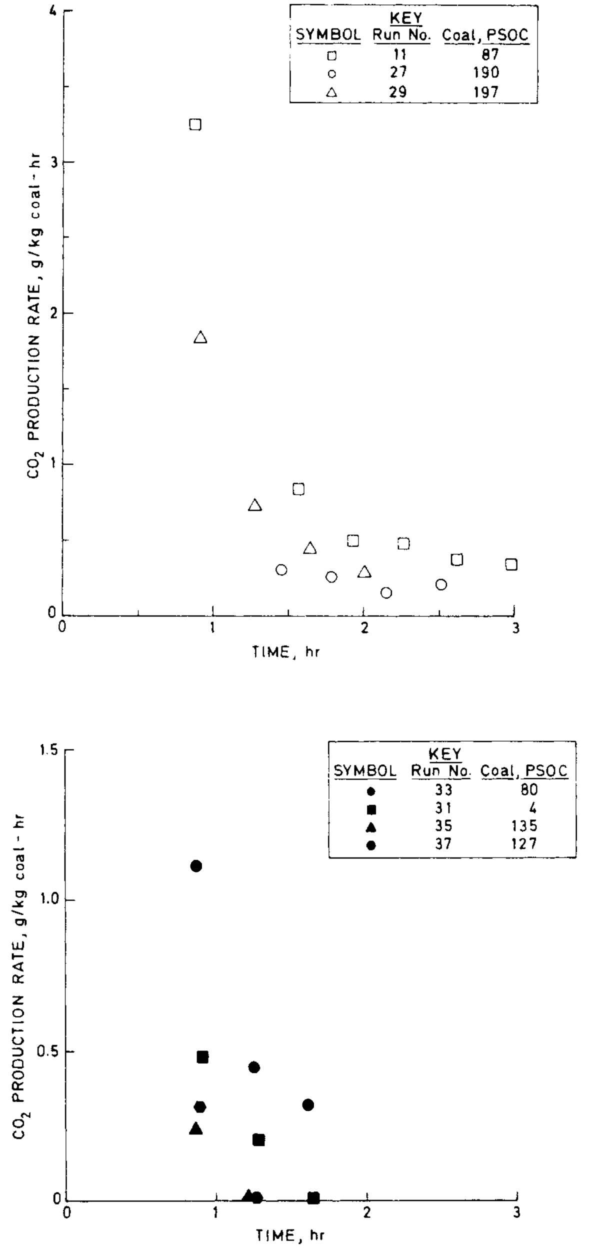

Figure 5. Rate of CO_2 production during the drying of several coals. Particle size: −6 +16 U. S. mesh; gas flow: 200 cm^3/min N_2; temperature: 150°C.

The rates of CO_2 formation during the isothermal portion of the drying process are given in Figure 5 for each of the seven coals, deleting the first 0.75 to 1.0 hour period during which the temperature of the coal bed was raised from 25 to 150°C. The rate data appear to follow a path of exponential decay, suggesting the coal drying model developed in the next section. The expectation that CO_2 production rates are highest for the coals which contain the largest initial oxygen content is tested in Figure 6 by crossplotting

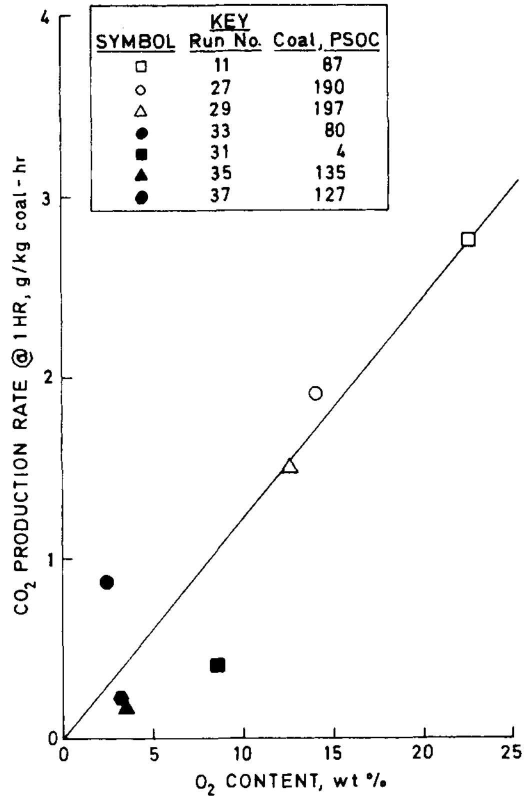

Figure 6. Effect of initial O_2 content on CO_2 production rate during drying.

rates obtained by interpolating Figure 5 for values at one hour. The result shows considerable scatter but a clear trend that includes the lignite. Low rank coals which typically contain more oxygen, more readily evolve CO_2 during drying than do those of high rank.

Drying Model

The macroscopic gas evolution rates observed in this study are probably summations of the decompositions of the several types of oxy-sites, since some chemical bonds decompose at elevated temperatures at faster rates than others. Rather than treat each type of oxy-group as a separate entity, the model developed here includes the assumption that the oxy-sites for CO_2 formation may be lumped into two types, each with a characteristic rate of decomposition to the CO_2 product. The reaction by path A is assumed to be first order with respect to concentration of site type A, and reaction via site B is treated as zero-order, assuming the concentration of type B sites overall to be relatively constant over the time interval of measurement. The sum of these two rates is

$$R = k_a S_a^o e^{-k_a t} + k_b \tag{1}$$

Evaluating Eq. 1 at $t = 0$

$$R^0 = k_a S_a^0 + k_b \tag{2}$$

TABLE 2. RUN CONDITIONS AND MODEL PARAMETERS FOR COAL DRYING-PARTICLE SIZE STUDY

Coal, PSOC No.	Drying Temp., °C	Particle Size, U.S. Mesh	Evolution Rate* g CO_2/kg coal·h R^o	R^∞	Rate Constant h^{-1} k_a
87	200	−6+16	3.0	0	0.49
87	200	−16+20	3.0	0	0.49
87	200	−20+30	3.0	0	0.49
190	175	−6+16	0.35	0	0.36
190	175	−20+30	0.35	0	0.36
190	175	−30+40	0.35	0	0.36

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* Initial rate computed for $t_o = 1$ h.

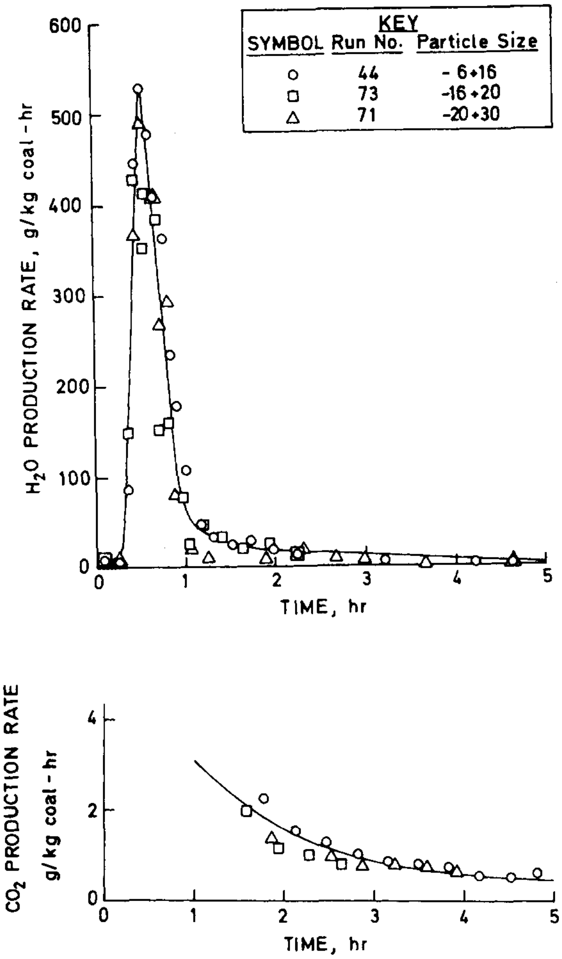

Figure 7. Effect of particle size on H_2O and CO_2 production rates. Coal: lignite, PSOC 87; temperatuare: 200°C; gas flow: 200 cm^3/min N_2.

and at $t \to \infty$:

$$R^\infty = k_b \tag{3}$$

Using these limiting rates notation, Eq. 1 becomes

$$R = R^\infty + (R^0 - R^\infty)\, e^{-k_a t} \tag{4}$$

This analysis may be extended to a fixed bed of coal particles by integrating the continuity equation to give the CO_2 production rate per weight of coal as

$$R = \frac{FC_E}{\rho AH} \tag{5}$$

At temperatures where gas evolution rates are relatively low, CO_2 would be evolved primarily by path A and the CO_2 evolution rate would simplify to:

$$R = R^0\, e^{-k_a t} \tag{6}$$

Effect of Particle Size and Temperature

To examine the applicability of the drying model to the fixed bed data obtained in this study, four coals have a wide range of chemical and physical properties were dried in the temperature range 150 to 300°C, using particle sizes in the range −6 to +40 U. S. mesh.

Drying conditions for the particle size study are listed in Table 2 and results are shown in Figures 7 and 8. No detectable CO is produced in this temperature range for either coal. The reactor temperature response, the H_2O production rate, and the CO_2 production rate are all independent of particle size for both coals tested. Apparently there exists little diffusional resistance to the evolution of gas products in this temperature range, suggesting that

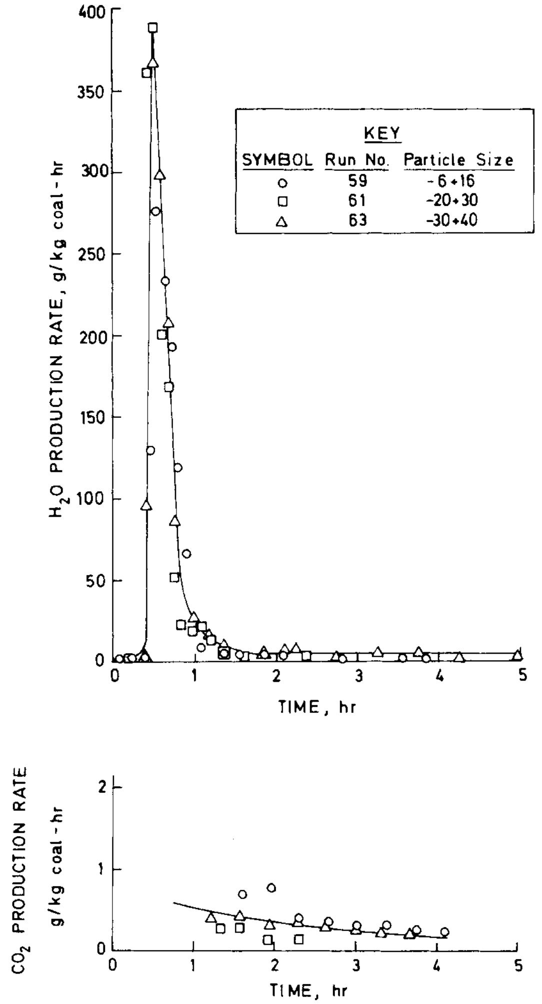

Figure 8. Effect of particle size on H_2O and CO_2 production rates. Coal: bituminous HVC, PSOC 190; temperature: 175°C; gas flow: 200 cm^3/min.

relatively low activation energies are to be expected in this study, the result of a chemical control regime characterized by weak surface bonds.

Drying conditions for the temperature study are listed in Table 3. Raising the temperature from ambient to a drying temperature of 150 to 300°C takes approximately 1 to 2 hours as shown in Figure 9, which gives representative temperature profiles for the four drying temperatures used in this study. Results for the lignite PSOC 87 are shown in Figures 10 and 11 terms of H_2O, CO_2, and CO production. The H_2O production rate reaches a maximum in approximately one-half hour for each run at a reactor temperature of 100°C. Since the H_2O rates above 100°C appear independent of reactor temperature, water evolution is primarily a physical process, evaporation. The additional H_2O evolved during the stepped drying of the lignite from 25 to 300° is small (Figure 1), and over 99% of the water produced is attributable to evaporation. Unlike H_2O production, CO_2 evolution (Figure 11) is an activated process, and CO production (Figure 11) also increases with temperature above 250°C. Below this temperature no measurable quantities of CO were observed. Similar qualitative results were found for the gas evolution rates of the bituminous coals PSOC 127, 190, and 197, although the rates vary in magnitude among the coals.

In summary, the experimental results show that: (1) H_2O production is primarily an evaporation process, independent of temperature above 100°C; (2) CO production is independent of CO_2 production, occurring primarily at or above 250°C. The experimental evidence of Figure 11 and similar data on PSOC 190 suggest that this transition temperature is between 200 and 250°C, just in the range reported for ring rupture during oxidation by Lahiri et al. (1959) and Kam (1975); (3) The ratio of CO_2/CO evolved is not constant during the drying process. For PSOC 87 for example (Figure 2) dried at successively higher temperatures, the CO_2/CO ratio increases with time as CO rates approach zero more quickly than CO_2 rates. Evidently, CO is the decomposition product of a more stable type of oxy-site than that which produces CO_2.

TABLE 3. RUN CONDITIONS AND MODEL PARAMETERS FOR COAL DRYING-TEMPERATURE STUDY

Particle size range: −6+16 U.S. Mesh
Atmosphere: Nitrogen flow at 200 cm^3/min

Coal, PSOC No.	Temp., °C	Evolution Rate* g CO_2/kg coal·h R^o	R^∞	Rate Constant, h^{-1} k_a
87	300	14.0	1.0	1.03
87	250	5.3	0.3	0.74
87	200	3.0	0	0.49
87	150	0.5	0	0.20
190	300	3.1	0.2	0.94
190	250	2.0	0.1	0.68
190	200	0.4	0	0.39
189	150	0.3	0	0.33
197	300	2.7	0.25	0.80
197	250	2.5	0	0.55
197	150	0.5	0	0.30
127	300	0.8	0.05	1.91
127	250	0.6	0	1.35
127	150	0.3	—	—

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* Initial rate computed for t_o = 1 h.

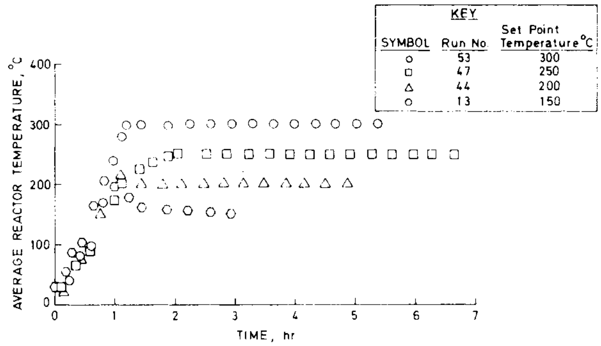

Figure 9. Reactor temperature during drying. Coal: lignite, PSOC 87; particle size: −6 +16 U. S. mesh; gas flow: 200 cm^3/min N_2.

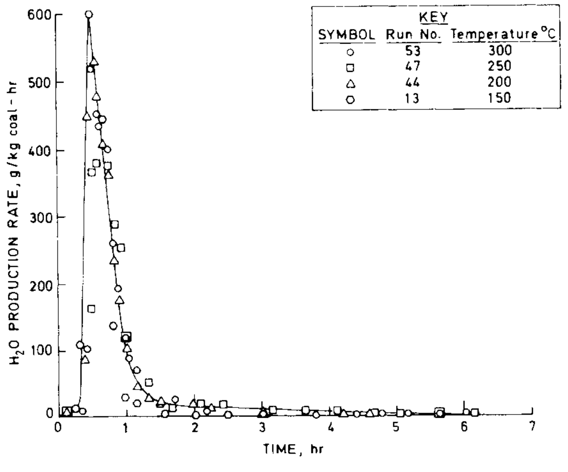

Figure 10. Effect of drying temperature on H_2O production rate. Coal: lignite, PSOC 87; particle size: −6 +16 U. S. mesh; gas flow: 200 cm^3/min N_2.

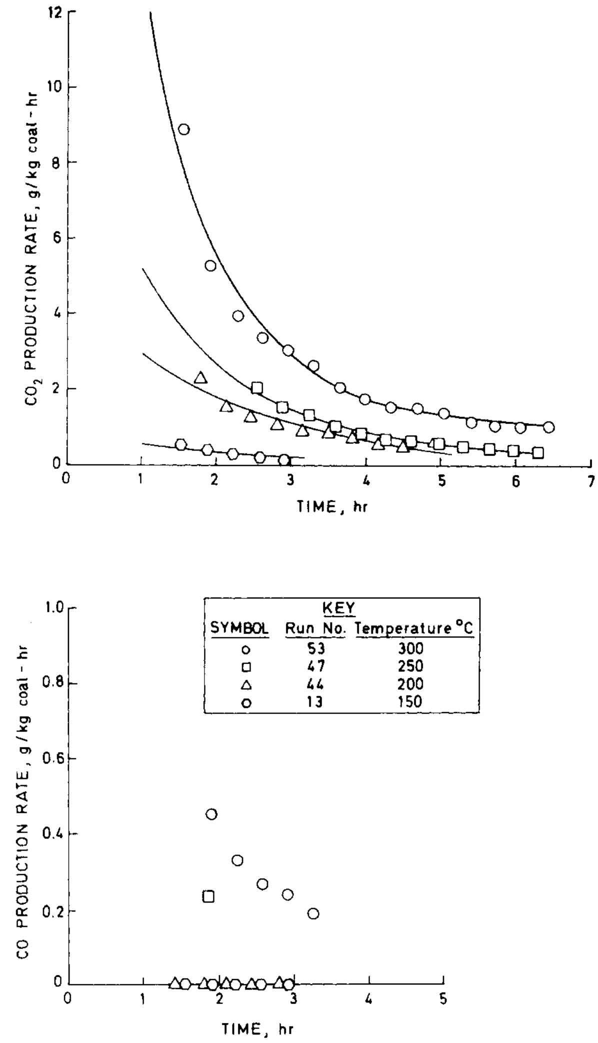

Figure 11. Effect of drying temperature on CO_2 and CO production rates. Coal: lignite, PSOC 87; particle size: −6 +16 U. S. mesh; gas flow: 200 cm^3/min N_2.

Rate Constants

To evaluate the constants in the rate expressions for CO_2 evolution Eq. 6 is applicable for $T < 250°C$ and Eq. 4 for $T > 250°C$. The reaction time must however be redefined to account for t_o, the period during which the coal is heated from room temperature to reaction conditions. The newly defined reaction time is $(t - t_o)$ where t is the time elapsed since heating began. Substituting into Eqs. 6 and 4:

$$R = R^o e^{-k_a(t-t_o)},\ , T < 250° \tag{7}$$

$$R = R^\infty + (R^o - R^\infty)e^{-k_a(t-t_o)}, T \geq 250°C \tag{8}$$

In logarithmic form:

$$ln\ R = -k_a t + [lnR^o + k_a t_o], T < 250°C \tag{9}$$

and

$$ln(R - R^\infty) = -k_a t + [ln(R^o - R^\infty) + k_a t_o], T \geq 250°C \tag{10}$$

A linear least squares fit of the data to these equations gives a slope of $(-k_a)$ and an intercept in terms of R^o, k_a, and t_o. The evaluation of k_a does not require an explicit solution for the induction time, but t_o is needed to solve for R^o. In the case of CO_2 production at 250°C or above, a value of the asymptotic rates of gas evolution

TABLE 4. ACTIVATION ENERGIES FOR CO_2 EVOLUTION DURING DRYING

Coal, PSOC No.	E, MJ/kmol
87	22 ± 7.6
190	15 ± 8.4
197	13 ± 6.7
127	17

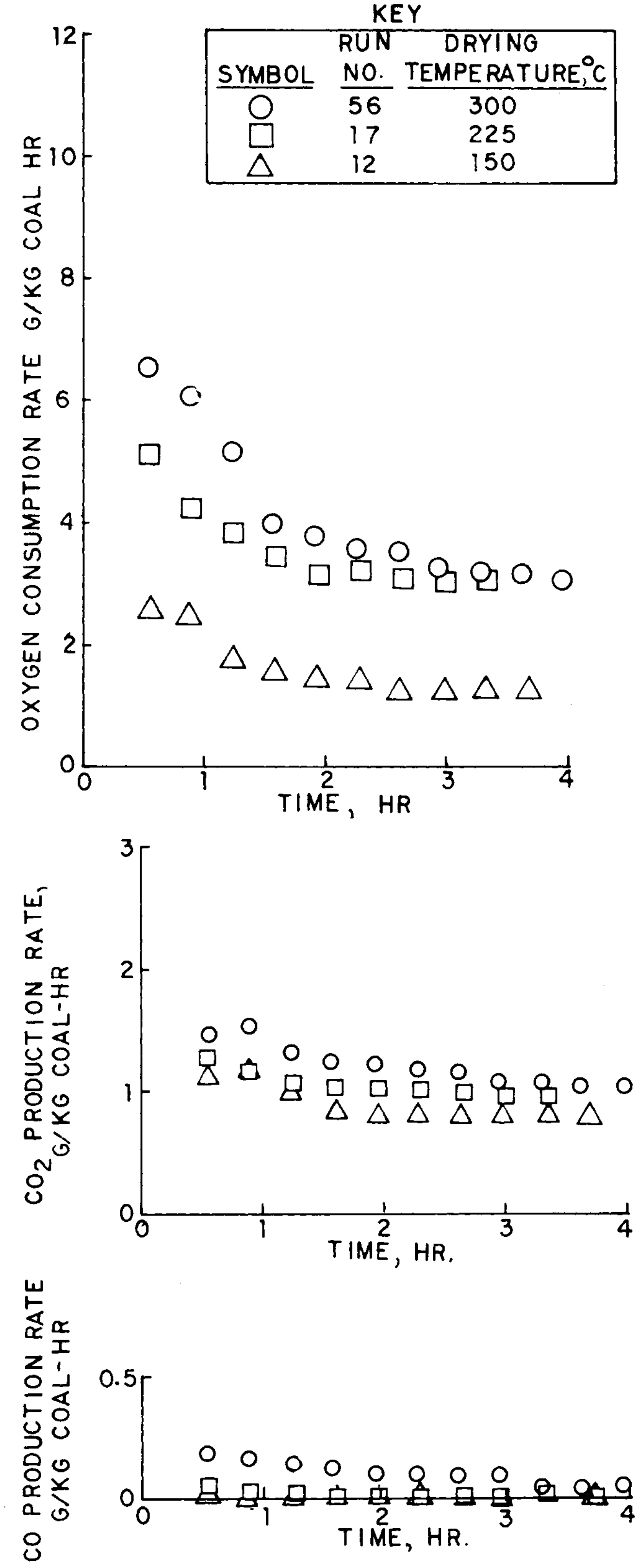

Figure 12. Effect of drying temperature on oxygen consumption and CO_2 and CO production rates of PSOC 87 at 150°C. Particle size: −6 +16 U. S. mesh; air flow: 100 cm^3/min.

TABLE 5. EFFECT OF DRYING TEMPERATURE ON PARTICLE SIZE DISTRIBUTION OF PSOC 87

Particle Size Range, U. S. Mesh	Untreated Coal		Dried 150°C*		Dried 225°C*	
	g coal	% in size range	g coal	% in size range	g coal	% in size range
+6	0.44	1.0	0	0	0	0
−6+16	44.43	98.7	38.48	95.8	27.13	89.0
−16+20	0.09	0.2	0.76	2.4	3.00	9.8
−20+30	0.01	0.0	0.16	0.5	0.13	0.4
−30+50	0.01	0.0	0.19	0.6	0.13	0.4
−50	0.02	0.1	0.21	0.7	0.11	0.4
Total	45.00	100.0	31.8	100.0	30.5	100.0

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* Subsequently oxidized @ 150°C.

R^{∞} was estimated separately by extrapolation of the experimental rate data. The rate constants are listed in Table 3 for all four coals together with the R^o values for $t_o = 1$ h, and the final reaction rates. The experimental scatter limits accurately to within ±10% on these results. The initial reaction rates for the lignite PSOC 87 are much higher than for the other three coals, reflecting the large oxygen content of this untreated coal. In agreement with the model, the asymptotic reaction rates R^{∞} are non-zero only in the 250 to 300°C range. Sample best fit curves for the CO_2 evolution from lignite are presented in Figure 11.

Activation energies for the rate constant for each of the four coals are listed in Table 4, with corresponding 95% confidence ranges. Such relatively low values, all in the range of 13 to 22 MJ/kmol, could be attributable to either diffusional effects or to the generally weak oxy-coal bonds on the coal surfaces which must be broken to evolve gases. The first of these possibilities was explored by looking for possible affects of particle size. Since no such affects were observed for PSOC 87 and 190 (Figures 7 and 8), the low activation energies are not the result of diffusional mechanisms.

With one exception, the CO production rates measured at 250 and 300°C showed selected non-zero data points, followed by several rates that are zero within the accuracy of the experiments. No CO was measured for PSOC 127 in the entire temperature range from 150 to 300°C, reflecting the low oxygen content of this particular coal. The single rate profile suggests that the CO production rate also falls exponentially with temperature; however, sufficient data are not available to compute rate parameters.

Effect of Drying on Subsequent Oxidation

The limited research reported in the literature on the effect of water on coal oxidation focuses on the effect of its presence on oxidation and not on the method or reaction conditions employed in its removal. Panaseiko (1974) compared the diffusion coefficients of oxygen in air and water, either of which the diffusing oxygen molecule may encounter in the pore structure of coal. These values differ by four orders of magnitude: 0.18 cm^2/s for air and only 2.3×10^{-5} cm^2/s for water. He therefore concluded that free water present within the coals inhibits oxidation, but that chemically bound water may enhance the oxidation process (due to hydrogen bonding). Menkovskii et al. (1975) oxidized coals at 20°C in a batch system and showed that the addition of various solvents such as water, salt water, or a 1% solution of water-glass to coals can inhibit oxygen consumption. They concluded that these solvents may even be helpful to minimize coal weathering.

To determine the effect of drying temperature on oxidation rate, three samples of lignite were dried in a nitrogen atmosphere at 150, 225, and 300°C, then cooled to 150°C and oxidized. The oxygen consumption rates for these three runs are given in Figure 12: there is a marked increase in rate with drying temperature. The initial reaction rates for oxidizing the coals at 150°C were approximately 4, 6 and 8 g O_2/kg coal-h for drying temperatures of 150, 225 and 300°C, respectively. A portion of this additionally consumed oxygen produces more CO_2 and CO. In fact, the coal drying temperature determines whether or not CO is produced in measurable quantities. After drying at 150°C, no CO was produced during oxidation, trace quantities were observed after drying at 225°C, and larger amounts during oxidation after 300°C drying. Since each coal was oxidized under the same conditions, these variations in oxidation rate are due to chemical and/or physical changes to the coal during drying.

A test to determine the physical changes occurring while drying at different temperatures is to measure the changes in particle size distribution after these drying/oxidation treatments. For this purpose the coal samples were crushed and sieved into various fractions: Table 5 lists a typical result of sieving 45 g of coal, the standard coal charge to the reactor. This sample is 98.7% in the desired −6 +16 U. S. mesh range with small amounts of both larger and smaller particles. The two coals dried at 150 to 225°C and oxidized at 150°C were also sieved into these various fractions. The Table 5 results show that drying and oxidation generally causes a reduction in average particle size with a concomitant increase in the superficial surface area of a sample. Drying at 225°C causes a 6.8% decrease in the population fraction that falls in the −6 +16 U. S. mesh range and an equivalent increase in the −16 +20 U. S. mesh size.

TABLE 6. CHEMICAL ANALYSES OF DRIED AND OXIDIZED COALS

Coal, PSOC No.	Temp., °C Drying	Temp., °C Oxidation	Heating Value* MJ/kg	Chemical Compositions* wt. % Carbon	Oxygen	Hydrogen
190	As Received		27.90	69.12	14.91	4.86
190	25 to 300	—	28.87	71.16	13.61	4.60
190	150	150	28.59	68.15	16.29	4.50
190	150	175	26.30	66.39	18.88	4.01
190	150	200	24.52	64.12	20.81	3.47
190	150	225	24.33	65.05	21.06	3.13
87	As Received		23.72	62.05	23.84	4.47
87	25 to 300	—	25.84	65.78	20.05	4.30
87	150	150	24.55	63.36	23.01	4.29
87	150	225	24.27	63.13	22.86	3.77
4	As Received		34.14	82.04	8.71	5.47
4	150	225	32.86	79.99	11.90	5.02

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* By Smith, Rudy Co., Philadelphia, PA.

TABLE 7. EFFECT OF OXIDATION TEMPERATURE ON HEATING VALUE

Oxidation Temp., °C	Heating Value, MJ/kg	Loss, %
150	28.59	0
175	26.30	8
200	24.52	14
225	24.33	15

Energy Losses

The practical goal of the mild oxidative pretreatment that precedes coal gasification is to reduce or eliminate the caking propensity of the coal. Since changes in the coal that result in a decrease in the heating value must be minimized, there is a tradeoff between operating severity to reduce caking and mild operation to minimize energy losses. Drying at lower temperatures also results in less carbonic gas evolution.

To determine the quantitative effects of drying and oxidation selected samples were analyzed for elemental compositions and heating values. These results are shown in Table 6 along with the drying and oxidation conditions for each sample. Under conditions of increasing severity of treatment the carbon content of the coal generally decreases as more carbonic gases are evolved, and the oxygen content increases in the form of cumulative adsorbed oxygen. Both processes reduce the coal heating value, the changes varying approximately linearly with both the carbon and oxygen contents. The effect of oxidation temperature on the heating value of bituminous coal PSOC 190 (-6 $+16$ U. S. mesh size) is given in Table 7. The heating value decreases 15 percent when pretreated at 225°C instead of 150°C, a loss probably unacceptable for the vast quantities of coal likely to be processed in this manner. The difference between 200°C and 225°C is not significant.

ACKNOWLEDGMENT

This research was funded by the U. S. Department of Energy, Fossil Energy Research Program, under Contract No. EX 76-S-01-2450.

NOTATION

A = cross-sectional area of reactor
C = concentration of carbon dioxide bulk gas
E = activation energy
F = volumetric flow rate
H = total reactor height
k_a = reaction rate constant for path a
k_b = reaction rate constant for path b
R = integrated total rate of CO_2 production by both reaction paths
S_a = concentration of reaction site a
T = temperature
t = time
t_o = period of time during which coal is heated from ambient to drying temperature

Superscripts

o = evaluated at $t = 0$
∞ = evaluated as $t \rightarrow \infty$

Subscript

E = evaluated at reactor exit

Greek symbol

ρ = fill density of bed

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Manuscript received October 27, 1980; revision received April 13 and accepted April 23, 1981